ATTACHMENT A

Research Proposal Submitted to

PHILIP MORRIS, U.S.A.

Title: Catalytic Oxidation

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Proposed Starting Date: July 1, 1989 or as soon after as possible

Proposed Duration: 36 months

Requested Amount: $330,000

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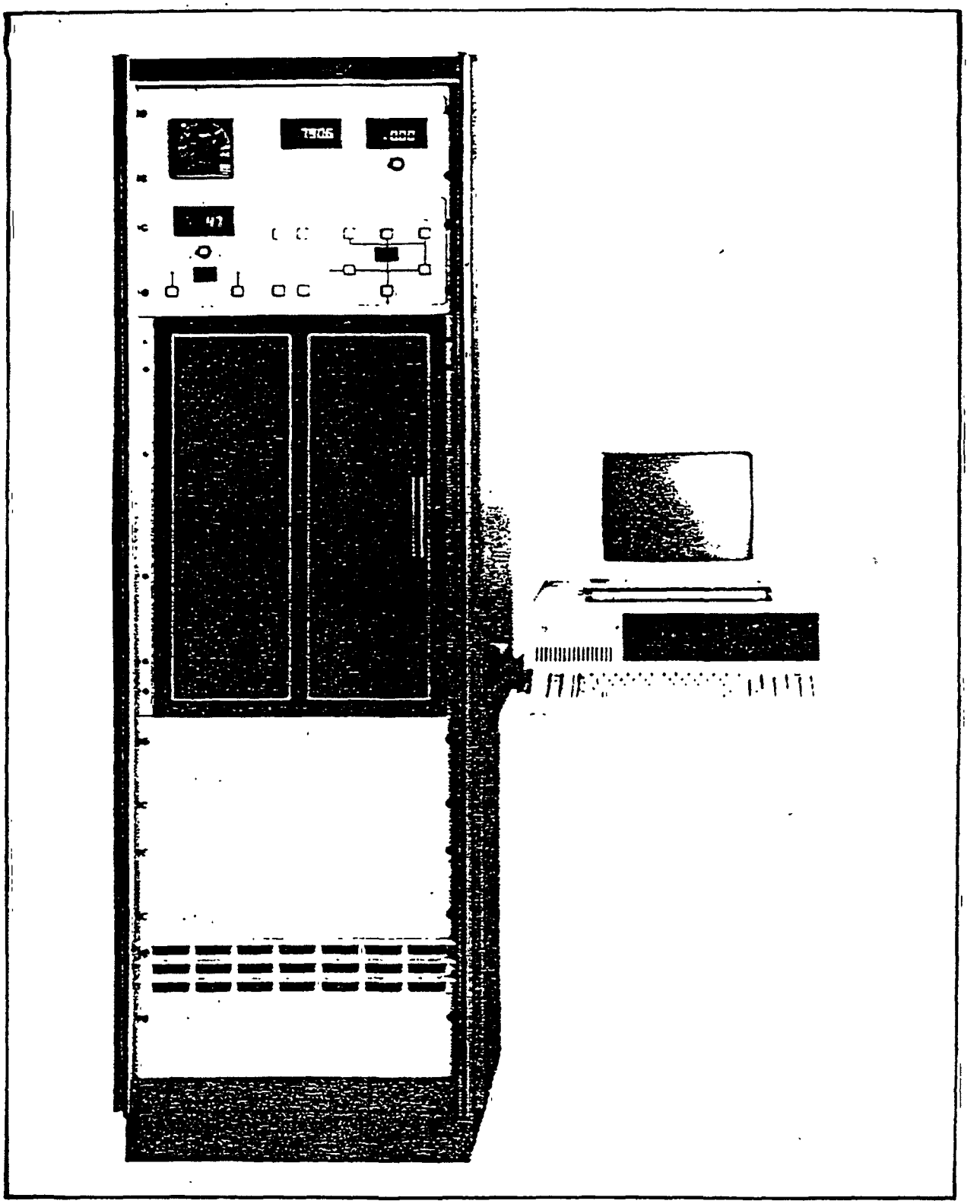

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OMNISORP 100CX CHEMISORPTION SURFACE AREA AND PORE SIZE ANALYZER

OMICRON TECHNOLOGY CORPORATION

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OMNISORP™-100CX ANALYZER

SYSTEM DESCRIPTION

SUMMARY DESCRIPTION

The Omnisorp™-100CX Analyzer is a fully computerized and automated double port instrument for determining both physisorption and chemisorption isotherms. One port is dedicated to physisorption work for precision characterizations of surface area and pore size for powders and solids with pore sizes from 2 to 2000Å in radius. The second port is for chemisorption analysis for surface areas, monolayer capacities and dispersions. The instrument includes a programmable furnace for chemisorption outgassing, reduction and sorption experiments to 450°C and for the outgassing of physisorption samples. It can be lowered to allow fast cooling of the sample.

The chemisorption port is designed to permit the reduction of the sample in a flowing stream of hydrogen. Prior to a chemisorption experiment, the sample can be outgassed in situ at temperatures up to 450°C in vacuum, followed by hydrogen reduction, if required, under a high flow of hydrogen gas that provides excellent mass transfer to the catalyst particles.

The analysis of a sample is fully automated, with computer-driven experimental control. All data is reduced by highly flexible computer software for presentation of tabular information and graphics as described on Page 4.

CONTINUOUS VOLUMETRIC METHOD. Isotherms are generated by up to 2000 data points for superior data resolution. The technique used to determine these isotherms (U.S. Patent No. 4,489,593) is different from competitive methods. In the Model 100CX, adsorbate gas is introduced to the sample continuously through a mass flow controller. Sample temperature is maintained from liquid nitrogen temperatures to 450°C, depending on the experiment. The rate of gas flow is maintained constant (better than 1%) throughout the experiment. The volume adsorbed or chemisorbed is calculated by integrating the flow rate over time, and subtracting the dead volume (manifold, holder, and sample volumes) which is determined by using helium.

STATIC VOLUMETRIC MODE. The unique adsorbate flow control features of the Model 100CX also enables the user to perform conventional Static Volumetric experiments. The mass flow controller can be programmed to provide virtually unlimited volume and equilibration time adjustment. No hardware or software changes are required.

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INTRODUCTION

Catalytic oxidation involving molecular oxygen (dioxygen) can be associated with one of two very general reaction pathways. In one a free radical organic intermediate is generated on the catalyst and then reacts with the dioxygen to give a hydroperoxy radical which reacts further to generate the various types of products obtained. Essentially all catalyzed oxidations of hydrocarbons take place by this general route.

In the second kind of reaction both the oxygen and the reacting substrate are adsorbed on the catalyst surface and oxidation occurs by the interaction of these adsorbed species. Over metal catalysts this occurs most generally by the insertion of an adsorbed oxygen atom into the substrate-catalyst bond. With oxide catalysts a loosely bound lattice oxygen usually interacts with the adsorbed substrate which results in a reduced oxide that is then reoxidized by the adsorption of dioxygen.

In the present discussion only the pathway involving the interaction of adsorbed substrates will be considered since this is the mechanism utilized in the catalytic oxidation of carbon monoxide.

The goal of this research is to find a catalyst capable of promoting the oxidation of carbon monoxide in low concentrations in air under ambient conditions in the presence of water, amines, and other materials present in cigarette smoke. Further studies will be conducted on the catalytic oxidation of acetaldehyde, acrolein, and other low molecular weight organic compounds present in passive cigarette smoke. In this phase, also, the aim will be to find a catalyst which will facilitate the complete oxidation of these materials as well as carbon monooxide to carbon dioxide under ambient to moderately mild conditions. Such catalysts would be beneficial in cleaning the air in conference rooms, lounges, etc. To be effective the

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catalyst would have to be quite efficient to operate under the extreme flow conditions needed for optimum air recirculation. It would also have to have to be resistant to catalyst inhibition by moisture, amines, and similar materials and have a reasonably long lifetime, as well. Such restraints are not unreasonable in catalytic processes.

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BACKGROUND

Because of its importance in automotive emission control the catalytic oxidation of CO has been extensively studied. All types of catalysts have been used for this reaction; metal single crystals, bulk metals, mixed metals, supported metals, oxides, mixed oxides and supported oxides. A complete review of this area is obviously not possible in the present context but some mention of representative results and conclusions found in the literature is appropriate. It should be kept in mind that since one of the primary reasons for examination of the catalytic oxidation of CO was to develop efficient automotive emission control systems a large proportion of the data in the literature is concerned with results obtained from high temperature reaction studies. Most of this type of information has been omitted in the present discussion which emphasized some of the more recent studies run at ambient or somewhat elevated temperatures.

One of the most commonly used catalysts for the oxidation of CO has been Pt. It has been reported, for instance, that on this catalyst there are two distinct types of sites present, each having different reaction kinetic characteristics. On one (Type I), which is probably comprised of face atoms on the metal surface, the reaction is first order in O_2 and negative first order in CO. On the other type of site (Type II), which is presumably the corner atoms on the metal particles, the rate is first order in CO and independent of O_2[1]. It was also found that the presence of CeO_2 increased Type II reaction characteristics. In addition five different types of CO adsorption states on Pt catalysts have been observed[2]. Yet, data obtained from oxidations run over metal single crystals provide a different impression of the active site involved in the reaction. This report concludes that CO oxidations run over all platinum metal catalysts

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is structure insensitive, i.e. that the reaction takes place with equal facility over all types of active sites[3,4]. To further confuse the matter other work on Pt single crystal catalysts indicated that increasing the number of kink or corner atoms increased the reaction rate[5] while spectral data indicated that O adsorbed on face atoms was more reactive toward CO than was O adsorbed on step or kink atoms[6]. This latter observation is supported by data obtained from reactions run over Pt(111) crystals[7] and supported Pt catalysts of different dispersions[8]. In the latter case it was found that CO oxidation proceeded more readily over catalysts having large metal particles and, thus, a higher percentage of face atoms on the metal surface.

It should be pointed out that these reactions were all run under different conditions. Some were run under very low partial pressures of the reactants while with others higher pressures were used. Reactant ratios were different in almost every study. Some investigations involved the used of a pulse or transient reaction approach while others used steady state reaction conditions. The temperatures used were certainly not uniform. Obviously, a study involving a consistent set of reaction conditions is warranted to clear up these apparently contradictory statements.

As was observed with supported Pt catalysts[8] the nature of the support can influence the reactivity of dispersed Pd catalysts. Pd/TiO_2 is an order of magnitude more reactive than is Pd/SiO_2 toward CO oxidation[9]. The structure insensitivity reported for Pd single crystal catalysts has been considered to be the result of a compensation effect on the overall reaction rates[10]. A similar explanation could be valid for Pt catalysts as well. Interesting spectral studies of the surface of Pd single crystal

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catalysts have indicated that the active site in CO oxidation over these species is a single Pd atom which adsorbs both the CO and an O atom[11].

As with Pt catalysts the activity of Rh/Al_2O_3 is promoted by the presence of CeO_2 but only under moderately oxidizing conditions, those with relatively low O_2 partial pressures. In the presence of a large excess of O_2, CeO_2 has no effect on the rate of CO oxidation over this Rh catalyst[12]. Under steady state conditions Ru catalysts are more reactive that either Pd or Rh containing materials[13].

Of the base metal catalysts, Cu is the most commonly used CO oxidation catalyst. In contrast to the reports of structure insensitivity with platinum metal catalysts, copper catalysts exhibit a very strong structure sensitivity with both single crystal and dispersed metal catalysts[14]. In the later case it was found that the rate of CO oxidation increased significantly with decreasing metal particle size on the catalyst[15] indicating that CO oxidation is probably occurring on the more coordinatively unsaturated surface atoms such as the corner or kink sites. Nickel catalysts have also been shown to be very effective for the low temperature CO oxidation[16]. The reactivity of these catalysts, though, is particularly sensitive to the nature of the surface oxide formed on the catalyst. An intermediate two-dimensional oxide is beneficial to the process while the more extensively oxidized three-dimensional oxide is inhibitory[17].

In addition to the metals discussed above a number of oxide catalysts have been found to be quite effective in the low temperature oxidation of CO. Perhaps the most effective material in this reaction is cobalt oxide[18] but, as already recognized, this material is deactivated by water vapor. Iron oxides have also been shown to be effective catalysts but only after

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they have been activated by heating under vacuum[19] which makes them impractical for common use. The various metal ferrites, however, do show significant activity and may be useful, practical catalysts[20]. Molybdenum oxide is also an effective CO oxidation catalyst[21] as are praseodymium oxide[22,23] and a number of metal-like carbides[24].

Oxide supported manganese oxide species have been investigated as potential CO oxidation catalysts but, except for the TiO_2 supported material, they form a strongly adsorbed intermediate which inhibits further reaction[25]. A Mn/Ag composite oxide is an effective catalyst with oxidation occurring via the Ag-O component and as the Mn-O the oxygen carrier[26]. A commercially available Mn/Cu oxide, hopcalite, presumably reacts in much the same way with Cu-O the oxidizing moiety. This material appears to be quite promising since it is effective at low temperatures and is reasonably resistant to catalyst poisoning[27-30]. A number of other composite Cu oxides have also been used for CO oxidation. Lanthanum cuprates are partially inhibited by CO_2[31]. The addition of Cu to Co oxide catalysts increases their resistance to SO_2 poisoning[32] while the addition of Cr to Cu oxides diminishes the inhibition by water noted with these materials[33]. Perhaps mixed Co oxides can be found with enhanced catalytic activity and minimal water inhibition. V_2O_5 is a relatively useful catalyst[34] particularly when supported on another oxide[35]. The introduction of Pt on the V_2O_5/Al_2O_3 catalyst markedly enhances its oxidation capability with oxidation taking place on Pt-O-V sites and the resulting Pt-V sites reoxidized by dioxygen[36].

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The adsorption of Cr, Ni, Cu, Fe, or Co ions onto oxidic materials produces reasonably effective oxidation catalysts[37,38]. Particularly promising materials have been prepared by the treatment of zeolites with Cu or Ni ions[39,40].

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THE PROBLEM

Even with the extensive literature available concerning the catalytic oxidation of CO there is little known about the molecular aspects of this reaction as it takes place on the different types of catalysts. Of particular interest in this regard is a basic knowledge of the nature of the oxygen chemisorption and, particularly on metal catalysts, the adsorption stoichiometry on the various types of active sites present on the catalyst surface. In hydrogen chemisorption some sites, the corner atoms, adsorb two hydrogen atoms while others only adsorb one. These sites react differently in alkene hydrogenation with the product obtained dependent, in part, on the number of hydrogen atoms present per site[41]. One would expect a similar effect in oxidation reactions. It is assumed that the surface metal atom/adsorbed oxygen atom ratio is one but there are reports of considerable discrepancies from this value. It is usually proposed that experimental values greater than one are the result of experimental error or extraneous reactions. The possibility of having more than one oxygen on a surface metal atom is not considered seriously. However, the coordinative unsaturation present on a number of different types of surface metal atoms is quite sufficient to promote the adsorption of either two oxygen atoms or an oxygen molecule as occurs with a number of homogeneous catalysts[42]. If this is found to be the case then it is reasonable to expect different reaction characteristics from such sites.

With oxide catalysts specific site oxygen adsorption stoichiometry is not usually a consideration since with these catalysts oxidation occurs via a transfer of a lattice oxygen to the substrate at one site followed by the

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oxidation of the reduced oxide by interaction with dioxygen elsewhere on the surface.

In order to design viable catalysts for the low temperature oxidation of CO one should know the nature of the active sites present on the catalyst surface which promote the reaction as well as the stoichiometry of substrate adsorption on each site. In addition the effect which various modifiers or catalyst supports can have on these factors is also of considerable importance. For comparison, the success of the related H_2/CO reactions has been due, at least in part, to the availability of just such data[43]. The conflicting reports mentioned above concerning the nature of the active sites present on platinum metals exemplify the problems faced in this area.

The primary goal of this research will be the development of a sufficiently detailed understanding of catalytic oxidation using adsorbed oxygen to permit the systematic preparation of catalysts capable of the low temperature oxidation of CO possibly in conjunction with the complete oxidation of low molecular weight organic compounds in low concentrations in air in the presence of materials such as water and amines. The initial utilization of such catalysts would be to remove CO directly from cigarette smoke so the working lifetime of the catalyst can be short. However, for other, more general, air purification purposes a long catalyst lifetime would be beneficial.

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PROPOSED RESEARCH

The proposed research will be concerned with the investigation of both dispersed metals and oxides as catalysts for the low temperature oxidation of CO. The dispersed metal studies will benefit greatly from the use of our Single Turnover (STO) characterization technique for such catalysts[41]. With this technique we have been able to identify and quantify five different types of active sites present on the surface of the metal particles present in the catalyst as well as to determine the effect which reaction variables[44], catalyst pretreatments[45] or the presence of modifiers[46] can have on the quantity and reactivity of these sites. Three of these identifiable sites are different types of corner atoms, one is composed of edge atoms, and the last appears to be comprised of the different types of face atoms present on the metal surface. Series of similar catalysts are available in which the various site densities change from catalyst to catalyst so the use of the entire series of catalysts to investigate a reaction can provide considerable information concerning the nature of the active site(s) involved in the reaction.

The initial thrust of this research will be to obtain a real estimate of the oxygen chemisorption stoichiometry on the various types of active sites present on supported metals. H_2/O_2 titrations have been extensively used to provide metal surface area data for supported metal catalysts but in every case the adsorption stoichiometry is assumed to be 1:1 for $O:Pt_s$[47,48], an assumption without real experimental verification. We propose to run these H_2/O_2 titrations over a series of STO characterized supported metal catalysts on which the H_2 adsorption stoichiometry for each type of site is known. These titrations are accomplished by passing

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successive pulses of known quantities of each gas over the catalyst in a vapor phase reactor and monitoring the effluent using gas chromatography and mass spectrometry.

The first gas pulsed in is adsorbed on the metal surface with the quantity adsorbed determined by passing several pulses over the catalyst until no change is observed between successive chromatographic peaks in the effluent and using the areas of these peaks and those from which adsorption occurred to calculate the amount of gas adsorbed. The initial pulses of the second gas react with the adsorbed material to produce water, freing the surface for adsorption of the second gas. If some of the adsorbed material is displaced from the catalyst it can be measured using a mass spectral analysis of the effluent peaks. From the size of the gas pulses, the amount of each gas consumed at each step, the amount of water formed, and, where it occurs, the amount of adsorbed gas displaced by the titrating gas, the amount of oxygen adsorbed on the metal surface can be determined. These results will be compared to the H_2 and O_2 chemisorption on the catalyst determined in the absence of other materials by use of the requested Omnisorp-100CX adsorption system. For a given catalyst the surface site densities and hydrogen chemisorption stoichiometries will be known so, from the amount of oxygen adsorbed in the pulse titration sequence the number of oxygen atoms present on each type of site can be determined. Using a series of catalysts having varying site densities will provide verification of the adsorption stoichiometry.

The initial work will be done using supported Pt catalysts for a number of reasons. 1) These catalysts have been extensively studied in our labs so we are familiar with their reaction characteristics. 2) A great

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deal of published data is available on the Pt catalysed oxidation of CO so comparison with literature results can be obtained at an early stage of the research to provide a base for future work. 3) As mentioned previously a number of apparent contradictions appear in the literature concerning the nature of the active sites on Pt catalysts which are involved in CO oxidation and this work will serve to clarify the problem. The results obtained using Pt will be extrapolateable to other metal catalysts as well.

Once the oxygen adsorption stoichiometry has been determined using Pt catalysts this technique will be extended to other catalytically active metals such as Pd, Rh, Ni, Co, Fe, and Cu. STO surface characterizations have been accomplished on Pd[49] and Rh[50] catalysts already and should be applicable for use on supported Ni, Co, and possibly Cu and Au, catalysts. It may not work on Fe catalysts because this catalyst is not capable of promoting alkene hydrogenation under ambient conditions. However, by the time Fe is investigated as a catalyst sufficient data should be accumulated using the other metals so a reasonable extrapolation for Fe should be possible. Here, too, the quantitative detemination of the chemisorption of the various active gases on these different supported metals will be valuable in determining the reaction mechanism occuring on these different catalysts.

Concurrent with the extension of the H_2/O_2 reaction data on other catalysts, the CO/O_2 reaction will be investigated over the STO characterized Pt catalysts. The extent of CO chemisorption on these catalysts in the absence of O_2 will also be determined using the Omnisorp-100CX. To determine the nature of specific site CO oxidations, pulse titrations of CO with O_2 and O_2 with CO will be run over series of

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catalysts. With the O_2 adsorption stoichiometry known for these catalysts, from the CO adsorption and reaction data the nature of the active sites which are promoting the CO oxidation can be determined. These results will be used to determine the general types of metal catalysts to use in a practical evaluation of a working catalyst since we have found that, in general, the type of site (corner, edge, or face) used for a reaction on one metal will also be used on others as well.

Since the infrared spectra of CO adsorbed on metals have been widely studied, spectral data will also be of importance in determining the adsorption and reaction characteristics of the various types of surface sites present on the metal. The data needed to relate specific IR bands with the different types of adsorbed CO molecules are available both in the literature and from our own work on supported metal carbonyl clusters[50-52]. Corner atoms should adsorb two CO molecules as a geminal dicarbonyl species having an IR doublet for the C=O stretch between 2100 and 2000 cm^{-1} while edge atoms only have sufficient coordinative unsaturation to adsorb one CO in a linear manner. This species will have a single IR band between 2050 and 2000 cm^{-1}. On face atoms bridging CO adsorption takes place with IR bands between 1800-1600 cm^{-1}. Extrapolation from the types of bands observed in the IR and the type of sites present on the catalyst is straightforeward qualitatively but even a semi-quantitative assessment is only possible when the IR data is used in conjunction with our STO results.

In addition to the C=O stretching frequencies mentioned above metal carbonyls also exhibit M-C bands which are even more useful when they can be detected. These bands are found in the 800-400 cm^{-1} region and are frequently masked by IR absorption bands of the support used for the

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catalyst. With proper care in the manipulation of the appropriate FTIR spectra, though, support absorption can be subtracted from the carbonyl/catalyst spectrum to provide usable data in the M-C region. The diffuse reflectance capability of our FTIR spectrophotometer is particularly useful for this type of study. By using our controlled atmosphere diffuse reflectance IR cell and appropriate spectral manipulations changes in both the M-C and C=O frequencies can be monitored[50] for the different types of CO adsorbed species under actual reaction conditions so the nature of the reacting species can be determined. In addition, unreactive adsorbed CO species can also be identified. Both of these facts are important in the development of an efficient useful catalyst.

The effect of different support materials on catalyst activity and the nature of the active sites can also be determined using the techniques described above. Of particular interest here will be the use of various zeolite supports for the metals and determining the effect of support pore size on the ease of reaction. Changes in site densities and reaction characteristics can be evaluated using the pulse reaction approach while the FTIR studies can be used to measure the effect on the strength of CO adsorption on the various sites. Treatment of the catalysts with modifiers such as water or amines prior to exposure to pulse reactions or IR analysis will provide data needed to evaluate the nature of the effect which such species may have on the outcome of the reaction.

A recent publication[53] reported that a Au/Fe_2O_3 catalyst is very effective for the low temperature oxidation of CO in the presence of water vapor. A computer assisted literature search covering the period from 1967

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gave only 19 references to the use of Au as an oxidation catalyst and 37 for Fe_2O_3. This indicates that neither Au nor Fe_2O_3 is effective by itself for this reaction so one has to conclude that there is a deffinite synergism between these two materials which promotes the efficient oxidation of CO. An extension of this work is indicated to determine whether the reaction is taking place on the supported Au particles as modified by the support material or if the Fe_2O_3 as modified by the electronic density of the Au is responsible for the reaction. To distinguish between these possibilities several Au catalysts supported on different types of oxides will be prepared along with a number of different metals supported on Fe_2O_3. Comparison of the STO, titration, and chemisorption data obtained with these catalysts and that found with the more standard catalysts described above will provide some indication of the active species present on the Au/Fe_2O_3 catalyst.

It has also been indicated that the method of preparation of this catalyst is critical for obtaining catalyst activity. The use of normal adsorption techniques for binding the metal salt to the oxide does not give very active catalysts. The most active species have been obtained when a mixture of Fe and Au salts are treated with base to precipitate a mixed hydroxide which is then calcined to give the mixed oxide. Reduction with hydrogen gives the supported Au metal. This preparation procedure will be used in the preparation of those catalysts used in this phase of the study. Comparison will be made in every case with comparable catalysts prepared using standard adsorption or ion exchange procedures.

In order to facilitate the reproducible large scale preparation of any effective catalysts which might be produced it is necessary to obtain as

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much information as possible concerning the processes taking place during the preparation of these catalysts. This will be accomplished by measuring the BET surface areas and micropore distributions of each catalyst at every stage of preparation. Appropriate chemisorption data will also be obtained where possible. In this way some of the physical and chemical properties of these catalysts which can affect catalytic activity can be monitored. These data can be obtained using the requested Omnisorp-100CX.

After the pulse reaction data are obtained from both the GC/MS analysis and the FTIR studies it will become possible to estimate the general type of catalyst needed for the efficient oxidation of CO. If the data indicate that the oxidation is proceeding primarily on the more coordinatetively unsaturated corner or edge atoms then the best catalyst to use would have to have very small metal particles to increase to relative number of such atoms present on the metal surface. If it were found that the reaction took place on face atoms as indicated by the previously mentioned single crystal data, then large metal particles would be preferred. While some initial studies using the platinum metals is necessary to develop a sound basis for further work, once the basic surface reaction characteristics have been identified further studies will be run on base metal catalysts. Again, preliminary work may require the use of specially reduced materials in order to gain an insight into specific metal reaction characteristics, but once this is obtained no special treatment of the catalyst will be performed in order to duplicate as close as possible the actual storage and reaction parameters of a potentially successful catalyst.

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The reaction efficiency of the selected catalytic materials will be determined by using them to promote the vapor phase oxidation of CO at ambient to moderate temperatures using O_2/CO mixtures with a wide range of partial pressures ultimately duplicating a mixture of air with a few hundred ppm of CO. Our vapor phase reactor system not only permits the analysis of reactants and products present in the gas stream after passage over the catalyst but also the introduction of various liquid vapors such as water or amines into the reactant stream to evaluate their effect on the reaction. Further, the oxidation reaction can be discontinued and an STO surface characterization run on the catalyst without removing it from the reactor or even exposing it to the atmosphere. This permits the evaluation of any changes in site density which may occur during the oxidation. Other techniques, such as Temperature Programmed Reductions, can also be applied to the catalyst to determine the extent to which it has become oxidized. The oxidation can be run for various lengths of time to see if excessive catalyst oxidation decreases its reactivity.

These steady state vapor phase reactions can also be run in the controlled atmosphere FTIR cell to determine the spectral characteristics of the adsorbed species present during the reaction and to see what changes, if any, are taking place as the reaction proceeds. The oxidation of the catalyst can be monitored using this procedure since CO adsorbed on an oxide will have different IR bands from those present on a metal surface.

As the pulse reactions on metal catalysts are being investigated a parallel approach concerned with the use of oxide catalysts will be initiated. Pulse titrations will be used with these catalysts not so much

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to determine any specific site densities but, rather to measure reaction and adsorption stoichiometry. While such studies will contribute to an understanding of the reaction characteristics of these oxide catalysts it is anticipated that the most significant data will be obtained using diffuse reflectance FTIR studies. These IR investigations will provide data related to the nature of the adsorbed CO species, and, by virtue of any changes observed on exposure to oxygen, the nature of the reactive species as well.

The oxides chosen for initial study will be those which have been described in the literature as having some effectiveness in CO oxidation. Of particular interest will be the copper, cobalt, iron, vanadium, molybdenum and manganese oxides both alone and supported on other materials. Mixed oxides will also be investigated. The spectral data obtained with the individual oxides will be of assistance in evaluating the effect of partial oxidation on the base metal catalysts. The use of FTIR data will enable us to determine, for instance, what is taking place on exposure of cobalt oxide to water vapor which decreases its catalytic activity. It is possible that in the presence of water the carbon dioxide which is formed is converted to a strongly adsorbed carbonate which blocks the oxide from further reaction. Surface IR data will be able to detect such a reaction. The minimizing of this water inhibition on copper oxides by the introduction of chromium[33] could be the result of decreasing the strength of carbonate adsorption. If this is the case, and IR studies would show if it were, then it may very well be possible to introduce a secondary ion into the cobalt oxide to accomplish the same thing by decreasing the strength of CO_2 adsorption.

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The mixed oxides will be studied to see if any data can be obtained which would be helpful in predicting the efficiency of such mixed oxides before they were prepared in order to avoid the use of an Edisonian approach to the finding of an efficient catalyst. Of particular interest here will be the commercial mixed Mn-Cu-oxide, hopcalite, which has been used for a variety of oxidations and appears to be reasonably effective for the removal of CO from air[27-30].

As a final note, the use of supported metal ions as oxidation catalysts will also be investigated, primarily by use of FTIR. Ions such as those of Ni, Cr, Co, Cu, and Fe will be adsorbed on supports such as silica, alumina and titania and evaluated for catalytic activity in a steady state reactor. Effective materials will be further investigated using the controlled atmosphere FTIR cell to determine the nature and reactivity of the adsorbed CO. Highly selective catalysts, inert to poisoning by larger molecules, could be prepared using the ion or ions found to be effective catalysts and supporting them on appropriate zeolite materials. Established preparation procedures can be used to insure that the active material is present only in the cages of the zeolites and, thus removed from exposure to the larger molecules present in cigarette smoke which could inhibit the activity of normal supported catalysts.

While it is difficult to predict what exactly will be accomplished in research of this nature during specific lengths of time it is the target for the first year of this research to gain a basic understanding of the CO/O_2 interaction on supported metals particularly those supported on Fe_2O_3 and from this understanding make a reasonable prediction of the type or types of catalysts worthy of future investigation. All work done at Seton

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Hall will be carefully coordinated with that done by Philip Morris so duplication will be avoided.

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R: REDACTED MATERIAL

Biographical Sketch

Dr. Robert L. Augustine, Professor of Chemistry
Department of Chemistry
Seton Hall University
South Orange, NJ 07079

Born: REDACTED

Education: B.S. Creighton University, Omaha, Nebraska, 1954
M.A. Columbia University, New York, NY, 1955
Ph.D. Columbia University, New York, NY, 1957

Honors:		
	1954	Baccalaureate degree, Magna Cum Laude
	1955-57	NIH Pre-doctoral Fellowship Recipient
	1977	Recipient McQuaid Medal for Distinguished Service, Seton Hall University
	1988	Recipient Joseph P. Hyman Award from North Jersey ACS for encouragement of graduate study of chemistry

Major Research Interest:

Surface characterization of dispersed metal particles; preparation of selective heterogeneous catalysts; development of synthetically useful heterogeneously catalyzed reactions.

Research and Professional Experience:

1988-	Chairman, Department of Chemistry, Seton Hall University
1987	Visiting Professor, Brunel University, Uxbridge, England
1977	Visiting Fellow, Princeton University, Princeton, NJ
1969-	Professor, Seton Hall University, South Orange, NJ
1962-69	Associate Professor, Seton Hall University
1961-62	Assistant Professor, Seton Hall University
1959-61	Assistant Professor, University of Texas, Austin
1957-59	Instructor, University of Texas

Dr. Augustine received his doctorate in 1957 from Columbia University for research in the area of natural product syntheses. Because of the need for a stereoselective route to a potential intermediate for the synthesis of quinine he became involved in research on the effect of reaction variables on the stereochemistry of catalytic hydrogenation. This interest in hydrogenation led to the publication in 1965 of the monograph "Catalytic Hydrogenation, Techniques and Applications in Organic Syntheses". For a number of years he has directed a research group involved with both synthetic organic chemistry and catalytic hydrogenation. In the past few years, though, his research activities have been almost exclusively in the area of heterogeneous catalysis. Since coming to Seton Hall he has supervised research which has led to the writing of twenty six doctoral dissertations and nine masters theses and the publication of over seventy research articles in the areas of organic synthesis, mechanism and utilization of catalytic hydrogenation, and catalyst comparisons. His present research group is comprised of six graduate students who are involved in a long range research effort leading to the development of a sufficient practical understanding of the details of catalysis to enable the practicing chemist to use catalytic reactions in a routine manner.

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This interest in the utility of catalysis is also manifested in his professional interests. He was a founding member of the New York Academy of Sciences Section of Catalysis (1968) and The Organic Reactions Catalysis Society (ORCS) (1973), two groups devoted primarily to the discussion of the practical, utilitarian aspects of catalysis. He is presently a member of the Advisory Board of the NYAS Section of Catalysis, and Past Chairman of ORCS. He has also served as a three time director of the Metropolitan Catalysis Society.

He has presented his research results at twelve invited symposia given, twenty six meeting presentations and over seventy seminars to academic institutions and industrial concerns.

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Publications (1979-1989)

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Reviews

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Facilities

The equipment available for this research includes flow reactor systems used for STO characterizations and steady state vapor phase reactions. One of these is interfaced with a VG Instruments SX200 Quadrupole Mass Spectrometer with microcomputer interface and control. Th gas chromatographs in these systems are also interfaced with microcomputers. They also have temperature control and temperature programming capabilities. Also available in the Chemistry Department is a Mattson Cygnus 25B FTIR spectrophotometer with ATR, diffuse reflectance ar controlled atmosphere cells.

Other pertinent equipment in these labs include:

Precision analytical balances.

Atmospheric pressure gas phase reactor.

Haake A80 refrigerated circulating bath.

300 cc Parr high pressure stirred autoclave.

Isolated high pressure facility to house the autoclave.

Other instrumentation in the Chemistry Department is listed on the following pages.

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Equipment List

Type of Instrument

NMR Spectrometer
- General Electric QE-300 Nuclear Magnetic Resonance Spectrometer
- Varian T-60A

Mass Spectrometer
- VG SX200 Quadrupole GC/MS

Infrared Spectrophotometers
- Mattson Cygnus 25-B FTIR
- Perkin Elmer 567
- Perkin Elmer 137, 237, 700, 710
- Beckman IR-4 and -5
- Perkin Elmer 1310 (2)

Ultraviolet-Visible
- Varian 2200
- Beckman Acta III
- Varian 219
- Beckman DK-2, DU, DB, etc. (many)
- Cary 11 (3) and 15 (2)
- Aminco DW-2

Atomic Absorption
- Jarrell-Ash 82-810
- Varian 1250
- GCA-McPherson
- Perkin-Elmer 303

ORD/CD
- Cary 60

High-resolution Luminescence (components)

Spectrofluorometers
- Aminco-Bowman with phosphorescence (2)
- Varian SF-330
- Spex Fluorolog with DATAMATE, polarization, absorbance
- Spex Fluorometer with photo-diode array
- Aminco SPF-500

Ortec Time Correlated Single Photon Fluorescence Lifetimes

Grating Monochromator (1m Spex) with Wavelength Drive

Photometer
- Turner Model 20

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Lasers
- Ar-ion CW
- He-Cd Cw
- Pulsed Nitrogen

Stopped-flow Spectrophotometers
- Durrum
- Aminco

Cryogenic Refrigerator System

X-Ray Emission/Diffraction
- GE XRD-5
- Canberra Electronics Multichannel Analyzer, etc.

Liquid Scintillation Counter
- Beckman 7500

Magnetic Susceptibility
- Gouy and Faraday

Centrifuges/Ultra Centrifuges
- Sorvall Refrigerated (2)

Polarography Systems
- PARC 364 plus electrode (2)

Electrochemical System
- PARC Components
- IBM EC 225, 220, 219, 229, 250

Bascom-Turner Intelligent Recorder

Nitrogen Box
- Plas Labs

Heat-conduction Microcalorimeter

Liquid Chromatographs
- High-Pressure Systems (components) (3)
- Medium-Pressure Preparative
- LDC Systems (3)
- Varian 5020
- High-pressure (components) with chemiluminescence detector

Chromatotron

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Gas Chromatographs
- Varian 3720 (2)
- Hewlett-Packard 6530
- Tracor
- Beckman
- Perkin-Elmer, Gow-Mac (5), Varian

Microcomputers, Minicomputers, I/O devices, etc (appx. 20)

Autoanalyzer
- Technicon Clinical

Electrophoresis Apparatus
- Perkin-Elmer 238

Shimadzu Isotachophoretic Analyzer

Differential Thermal Analyzer
- Fisher Quantitative
- Fisher 360
- Dupont 900

BET Surface Area

Scanning Calorimeter
- Perkin-Elmer DSC 1-B

Network Analyzer
- Hewlett-Packard 8410A, 8411A, 8413A, 8690B, 8740A, 8741A, 8743A, 618C, 626A

Dielectric Spectrometer Components
- Tektronix TDR Sampling Oscilloscope Components

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BUDGET

Item	Year I	Year II	Year III
Salaries and Wages			
P.I. 1 month Summer Salary	7,050	7,600	8,200
Post-Doctoral Associate	18,000	19,000	20,000
Pre-Doctoral Student Stipend	10,800	11,400	12,000
TOTAL, Salaries and Wages	35,850	38,000	40,200
Fringe Benefits 15% P.I. Salary	1,058	1,140	1,230
Travel	4,000	4,000	4,000
Supplies	6,134	5,850	5,641
Permanent Equipment	89,835	0	0
Pre-Doctoral Tuition	6,000	6,500	7,000
Total Direct Costs	142,877	53,490	56,071
Indirect Costs 64.5% Salaries and Wages	23,123	24,510	25,929
TOTAL	166,000	80,000	84,000
Total Requested	$330,000		

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Budget Justification

Permanent Equipment

Omnisorp-100CX Analyser and ancillary equipment as per attached quote $71,205 Less 10% Academic Discount	64,085
IEC Centra-4 Benchtop Centrifuge, rotors, shields, and tubes	2,000
Lindburgh Muffle Furnace	750
Gow-Mac 69-560P capillary GC with micro TC detector, columns and recorder	9,500
Omega FMA-DV flow controller with control valves and transducers	8,000
Omega CN-2010 programmable temperature controller with auxiliary relay etc.	1,000
Rheodyne 7010 sample injection valve with sample loops	500
Epson Equity II+ microcomputer with hard disk, monitor, printer, math coprocessor, and 12 bit A/D converter/ multiplexer board with digital outputs	4,000
TOTAL	89,835

Permanent Equipment

The Omnisorp-100CX chemisorption surface area and pore size analyser is a fully computerized and automated instrument for the determination of the extent of both physisorption and chemisorption on catalyst surfaces. A complete system description of this instrument is attached to this proposal. This instrumentation is important for the success of the proposed research for many reasons. In the first place accurate, quantitative data for the chemisorption of the reactive gases, H_2, O_2, and CO on the many catalytically active materials which will be studied in this work is critical to the determination of the oxidation characteristics of these catalysts as described above in the various parts of the Proposed Research section. The Omnisorp-100CX is capable of providing this information conveniently and reproducibly. The system has computer controlled catalyst pretreatment capabilities which are needed to obtain reliable and reproducible adsorption data. Standard catalyst pretreatment procedures prior to chemisorption measurement usually include the heating of the catalyst in O_2 for a period of time followed by further heating in H_2 to effect complete reduction. The H_2 is then removed by further heating under vacuum. After cooling the extent of chemisorption is determined. The pretreatment conditions available with the Omnisorp-100CX include the

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timed heating of the catalyst sample either by itself or in a gas stream under high vacuum at controlled temperatures ranging from -80° C to 450° C.

We do not, at present, have such capability so the chemisorption data we obtain is not very reliable nor reproducible. This has not been a serious constraint till now in that we have usually only worked with a few catalysts at a time and could afford to spend the time needed to repeat chemisorption determinations until reproducibility was obtained. With the large number of catalysts anticipated to be involved in the proposed research such an approach would be quite time consuming.

In addition to the quantitative chemisorption capabilities of the Omnisorp-100CX it can also be used to for BET surface area determinations on solids as well as the distribution of pore sizes in the range of 2 to 2000 Å. Being able to determine these parameters at each stage of catalyst preparation will be essential in developing reproducible preparation conditions for any catalysts found to be effective and requiring large scale preparations for further development. This capability will be especially important with the development of the co-precipitated hydroxides as catalyst precursers. Correlating catalyst activity with mixed hydroxide precipitation techniques and the time and temperature used for calcining as well as the hydrogen reduction step is essential for effecient catalyst development. The availability of bulk and metal surface areas and pore size distributions will provide detailed information concerning catalyst composition and morphology. Correlating these factors with catalyst activity will provide a sound basis for the large scale preparation of viable catalysts.

A centrifuge is needed for the separation of the adsorbed salt on the oxide from the mother liquor used in its preparation. It is particularly critical for the isolation of the co-precipitated hydroxides which will be almost impossible to filter.

A muffle furnace with reasonable temperature control is needed for the calcining of the catalyst samples.

As discussed in the Proposed Research Section a combination pulse and steady state vapor phase reactor system is needed to incorporate with the controlled atmosphere FTIR cell. The rest of the equipment requested will provide for this need. The flow controller with multiple control valves is needed to maintain constant gas flows during the reactions and the sampling valve is required for injection of known gas quantities into the reactor.

The microcomputer will be interfaced with the GC, temperature controller, and flow controller to provide digital data acquisition, evaluation and storage capability as well as the ability to monitor the temperature and gas flows during the reaction run to provide assurance that these factors have not changed during the time the reaction was being run. The 12 bit A/D converter provides sufficient resolution for these purposes while the multiplexer capability permits the shifting of the input from the GC to the various controllers at appropriate times. Multitasking is also possible with the 80286 microprocessor in the Equity II+.

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Salaries

Salary support is requested for a post-doctoral associate and a pre-doctoral graduate student for the full year. Tuition for graduate credits is also requested for the predoctoral student. It is anticipated that the post-doctoral associate will have experience in working with oxides and will, therefore, be working almost exclusively on the use of oxidic materials as oxidation catalysts. The pre-doctoral student, on the other hand, will primarily be working on the more theoretical aspects of adsorption and reaction stoichiometry and the like. All salaries are in accord with current University guidelines. The P.I. summer stipend is 1/9 of his academic year salary.

Materials and Supplies

Funds are requested for the purchase of high purity gases, metal salts and oxides and other catalysts and catalyst precursors.

Travel

Funds are requested for travel to scientific meetings and to present our results to Philip Morris personnel on a regular basis. Travel is regulated in accord with current University policy.

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